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(71) Applicant (for all designated States except US):
NANOPOL INC. [KR/KR]; 974-7, Yangduk-dong,
Hoewon-gu, Masan, 630-728 Kyungnam (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LEE, Jeong-Sam

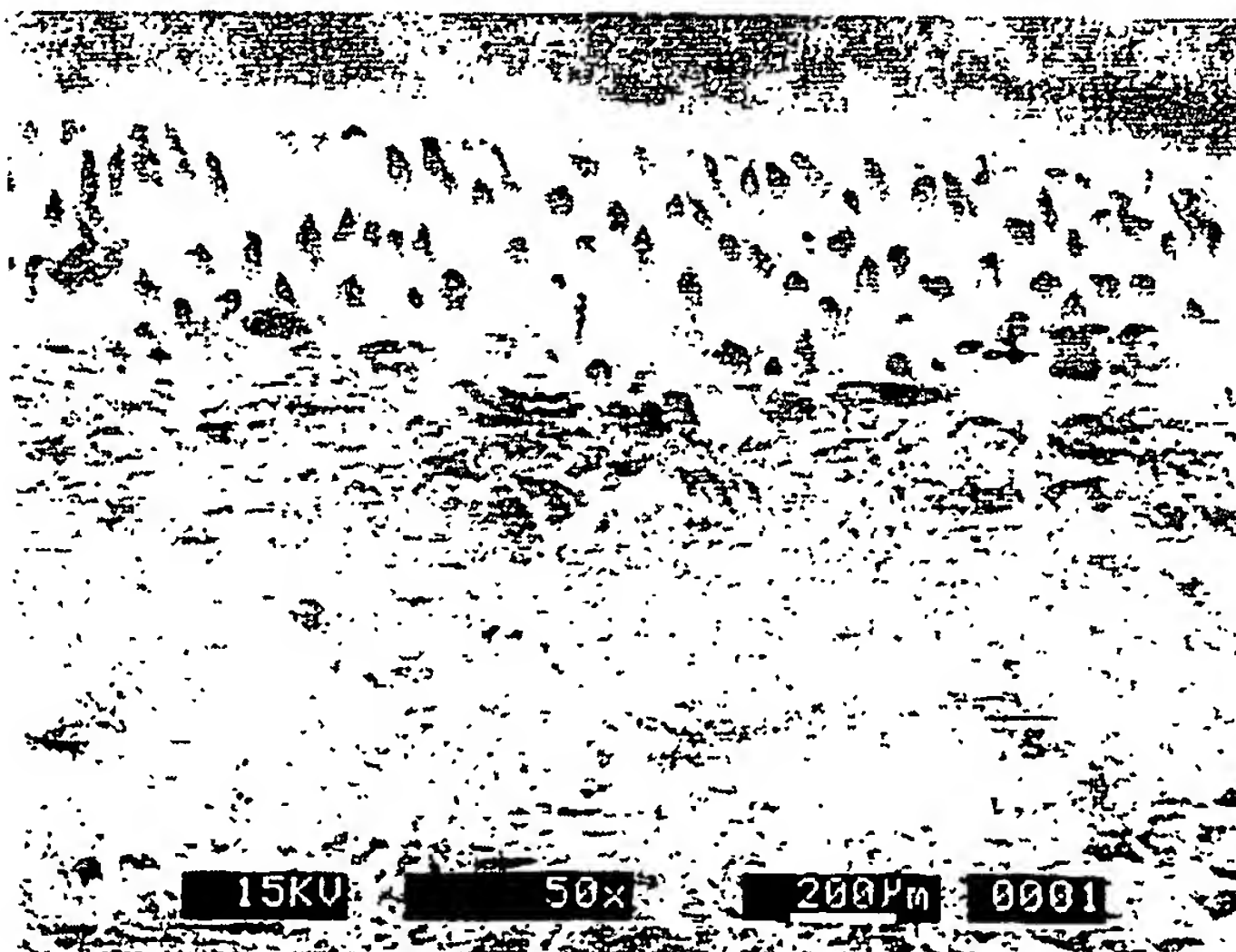
[KR/KR]; Neospot Apartment 101-2606, Bujune-dong,
Pusanjin-gu, 614-030 Pusan (KR). YU, Jae-Hong
[KR/KR]; 25/2, 67-10, Chilsan-dong, Dongrae-gu,
607-030 Pusan (KR). CHO, Seong-Mo [KR/KR]; 7/2,
627-7, Munhyun 2-dong, Nam-gu, 608-042 Pusan (KR).
BAE, Sang-Sik [KR/KR]; Haewoundae Whamok-Town
101-107, 1310, Chwa-dong, Haewoundae-gu, 612-030
Pusan (KR). KIM, Hyung-Seoung [KR/KR]; Hanil-Town
2nd 204-1006, 64-1, Yangduk-dong, Hoewon-gu, 630-490
Pusan (KR).

(74) Agent: SHIN, Young-Moo; Samdo building 4th floor,
1-170, Soonhwa-dong, Chung-gu, 100-130 Seoul (KR).

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(54) Title: SYNTHETIC LEATHER MANUFACTURING METHOD USING AQUEOUS POLYURETHANE DISPERSIONS



(57) Abstract: Disclosed is a method for preparing a synthetic leather, in which a composition including an anionic or cationic aqueous polyurethane dispersion, a water repellent, an emulsifier, an antifoamer and an inorganic filler is impregnated into a substrate, and coated on the substrate, the impregnated and/or coated substrate being then coagulated to form a synthetic leather internally provided with numerous closed cells and having a smooth surface. The aqueous polyurethane-based synthetic leather is obtained by impregnating a composition comprising 100 parts by weight of an aqueous polyurethane dispersion, 0.1 to 5 parts by weight of a water repellent, 0.1 to 8 parts by weight of an emulsifier, 0.1 to 1 part by weight of an antifoamer, and 0.1 to 5 parts by weight of an inorganic filler into

a substrate, coating the foamed or defoamed composition on the substrate, and coagulating the coated substrate with a coagulating solution, wherein aqueous polyurethane dispersion is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group, wherein the coagulating solution is selected from the group consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and mixtures thereof.

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SYNTHETIC LEATHER MANUFACTURING METHOD USING AQUEOUS POLYURETHANE DISPERSIONS

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TECHNICAL FIELD

The present invention relates to a synthetic leather manufacturing method using an anionic or cationic aqueous polyurethane dispersions and, more particularly, to a synthetic leather manufacturing method, in which a composition comprising an anionic or cationic aqueous polyurethane dispersion, a water repellent, an emulsifier, an antifoamer and an inorganic filler is impregnated into a substrate such as nonwoven or woven fabric etc. and/or coated on the impregnated substrate, and then coagulated to form a synthetic leather internally provided with numerous closed cells and having a smooth surface.

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BACKGROUND ART

Generally, synthetic leathers are prepared from a polyurethane, which is excellent in chemical and physical properties, inter alia, chemical resistance and softness.

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U.S. Patent No. 3,208,875 discloses a method for preparing a synthetic leather internally provided with numerous closed cells and having a coagulated surface layer, in which a solution of polyurethane in an organic solvent is coated on a nonwoven fabric and the polyurethane-coated nonwoven fabric is then passed through a coagulation bath normally containing water as a coagulating solution compatible with

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the organic solvent used to dissolve the polyurethane but incompatible with the polyurethane, allowing the organic solvent included in the solution coating to be diffused into the coagulating solution of the coagulation bath. This method, however, uses an excess of an organic solvent that is relatively toxic and has a high boiling point to cause environmental pollution.

To solve this problem, a growing interest has been taken in the methods for preparing a synthetic leather using an aqueous polyurethane dispersions.

U.S. Patent No. 4,171,391 discloses a method for preparing a synthetic leather using an aqueous polyurethane dispersions. This method is, however, undesirable since it has a limit on controlling the structure of cells (e.g., size and density of cells) and utilizes acetic acid as a coagulating solution whose unique spicy odor is not easy to remove but has to be separately removed from the final product. Moreover, the method takes too much time in coagulation that the productivity may be deteriorated.

Another method for preparing a synthetic leather with reduced complexity of the process, especially, reduced time for coagulation is disclosed in U.S. Patent No. 4,332,710, characterized by using a heat-coagulating agent that generates an acid by heat to promote coagulation. This method is disadvantageous in that the use of the heat-coagulating agent deteriorates the storage stability of aqueous polyurethane dispersions. U.S. Patent No. 5,460,873 discloses still another method for preparing a synthetic leather using a physical foaming machine to cause production of cells under mechanical stirring at high speed. This method, however, involves some problems in that the open cells cover the surface of the product, such product being inadequate for use as a synthetic leather due to its coarse surface, and that the conventional process of manufacturing the synthetic leather is unusable since the

method requires a separate drying facility.

Accordingly, there is still a need of a novel method for preparing a synthetic leather environment-friendly and excellent in properties and productivity.

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DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a aqueous polyurethane dispersion composition suitable for a synthetic leather.

It is another object of the present invention to provide a method for preparing a synthetic leather of good properties which is internally provided with numerous closed cells and almost destitute of open cells on the surface.

It is still another object of the present invention to provide a method for preparing a synthetic leather internally provided with cells of which the size, shape and distribution are controllable depending on the condition of the coagulation bath containing coagulation solution.

To achieve the objects of the present invention, there is provided an aqueous polyurethane dispersion composition for a synthetic leather, comprising: 100 parts by weight of an aqueous polyurethane dispersion, of which the main chain is covalently bonded to anionic groups including a carboxyl group or a sulfonate group, or cationic groups including a tertiary amine group : 0.1 to 5 parts by weight of a water repellant: 0.1 to 8 parts by weight of an emulsifier; 0.1 to 1 part by weight of an antifoamer; and 0.1 to 5 parts by weight of an inorganic filler.

In another aspect of the present invention, there is provided aqueous polyurethane-based synthetic leather that is obtained by impregnating the composition comprising 100 parts by weight of an aqueous polyurethane dispersion.

0.1 to 5 parts by weight of a water repellent, 0.1 to 8 parts by weight of an emulsifier, 0.1 to 1 part by weight of an antifoamer, and 0.1 to 5 parts by weight of an inorganic filler into a substrate, and/or coating the defoamed or foamed composition on the substrate, and then coagulating the impregnated and/or coated substrate with a coagulating solution, wherein the aqueous polyurethane dispersion is obtained by dispersing a polyurethane in water of which the main chain is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group, wherein the coagulating solution is selected from the group consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and mixtures thereof.

In further another aspect of the present invention, there is provided a method for preparing a synthetic leather from an aqueous polyurethane dispersions, comprising the steps of: (a) preparing the composition comprising 100 parts by weight of an aqueous polyurethane dispersions, 0.1 to 5 parts by weight of a water repellent, 0.1 to 8 parts by weight of an emulsifier, 0.1 to 1 part by weight of an antifoamer, and 0.1 to 5 parts by weight of an inorganic filler, and subjecting the composition to mechanical foaming or defoaming, wherein aqueous polyurethane dispersions of which the main chain is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group; (b) impregnating the aqueous polyurethane dispersion composition into a substrate including a woven or nonwoven fabric; (c) coating the substrate obtained in step (b) with the foamed or defoamed composition in step (a); (d) coagulating the substrate obtained in step(c) with a coagulating solution selected from the group

consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and mixtures thereof; and (e) subjecting the coagulated substrate to a post-treatment including washing, and drying, etc.

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BRIEF DESCRIPTION OF DRAWINGS

Figures 1 to 19 present microscopic photographs showing enlarged cross sections of the synthetic leathers prepared in accordance with Examples 1 to 19 of the present invention.

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BEST MODE FOR CARRYING OUT THE INVENTION

An aqueous polyurethane dispersion composition for synthetic leather according to the present invention comprises 100 parts by weight of an aqueous polyurethane dispersion of which the main chain is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group; 0.1 to 5 parts by weight of a water repellant; 0.1 to 8 parts by weight of an emulsifier; 0.1 to 1 part by weight of an antifoamer; and 0.1 to 5 parts by weight of an inorganic filler.

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An aqueous polyurethane-based synthetic leather according to the present invention is prepared by impregnating a substrate with a composition comprising 100 parts by weight of the aqueous polyurethane dispersion of which the main chain is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group, 0.1 to 5 parts by weight of a water repellant, 0.1 to 8 parts by weight of an emulsifier, 0.1 to 1 part by weight of an

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antifoamer, and 0.1 to 5 parts by weight of an inorganic filler, coating the foamed or defoamed composition on the substrate, and coagulating the coated substrate with a coagulating solution selected from the group consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a
5 mixed solution of acid and base, and mixtures thereof.

The anionic or cationic polyurethane dispersion is an aqueous polyurethane dispersion of which the main chain is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group, as disclosed in U.S. Patent Nos. 2,968,575 and 4,171,391 that are incorporated
10 herein by reference. That is, the aqueous polyurethane dispersion is obtained by a method in which an aqueous dispersion type polyisocyanate including an ionic charged group to allow self-emulsification is prepared by the condensation reaction between isocyanate, diol, polyol, and ionic chain extender, dispersed in water, and then subjected to polymerization reaction using a polyamine type chain extender. The
15 isocyanate as used in preparation of the polyisocyanate includes aromatic or aliphatic diisocyanates and a mixture thereof. Specifically, the isocyanate is selected from the group consisting of tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, meta-phenylene diisocyanate, biphenylene-4,4'-diisocyanate, methylenebis(4-phenyl diisocyanate), 4-chloro-1,3-phenylene diisocyanate, naphthalene-1,5- diisocyanate,
20 tetramethylene-1,4- diisocyanate, hexamethylene 1,6- diisocyanate, decamethylene-1,10- diisocyanate, cyclohexylene-1,4- diisocyanate, methylenebis(4-cyclohexyl isocyanate), tetrahydronaphthylene diisocyanate, isophoron diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), and mixtures thereof. The isocyanate is preferably hexamethylene-1,6-diisocyanate, isophoron diisocyanate, cyclohexylene

1,4-diisocyanate, or 4,4'-methylenebis(cyclohexyl isocyanate).

Examples of the polyol as used in preparation of the polyisocyanate include a polyester polyol or a polyether polyol. The polyester polyol is usually obtained by condensation reaction between a dicarboxylic acid compound and a diol compound.

- 5 Examples of the dicarboxylic acid compound as used herein include succinic acid, glutaric acid, adipic acid, suberic acid, azelanic acid, sebacic acid, dodecane dicarboxylic acid, hexahydrophthalic acid, isophthalic acid, terephthalic acid, ortho-phthalic acid, tetrachlorophthalic acid, 1,5-naphthalene dicarboxylic acid, fumaric acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, and
- 10 tetrahydrophthalic acid. Examples of the diol compound as used herein include ethyleneglycol, propyleneglycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, diethyleneglycol, dipropyleneglycol, triethyleneglycol, tetraethyleneglycol, dibutyleneglycol, 2-methyl-1,3-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, and 1,4-cyclohexanedimethanol. The customary
- 15 example of the suitable polyether polyol include polyethyleneglycol, polypropyleneglycol, and polytetramethyleneglycol. The molecular weight of the polyol is in the range from 400 to 10,000 and preferably from 400 to 3,000. The ionic chain extender for self-emulsification of the polyisocyanate can be either an anionic chain extender or a cationic chain extender. The suitable anionic chain extender as
- 20 used herein is a compound containing a carboxyl group or a sulfonate group, such as 2,4-diamino-5-methylbenzenesulfonic acid and 2,2-dimethylolpropionic acid. The suitable cationic chain extender as used herein is a tertiary amine diol or diamine compound, such as methyldiethanolamine. The amount of the ionic chain extender is in the range of 1 to 25 wt.%, and preferably 1.5 to 5 wt.% based on the total weight of

the polyurethane. A neutralizing agent is used to convert the anionic or cationic groups covalently bonded to the main chain of the polyurethane to a salt in order to increase dispersability in water for self-emulsification. Examples of the neutralizing agent for an anionic polyurethane include trimethylamine, triethylamine, triisopropylamine, tributylamine, N,N-dimethylcyclohexyl, N,N-dimethylaniline, N-methylmorpholine, N-methylpiperazine, N-methylpyrrolidine, and N-methylpiperidine. Examples of the neutralizing agent for a cationic polyurethane include acids such as phosphoric acid and acetic acid. The amount of the neutralizing agent is stoichiometrically more than 80% based on the ionic group. The isocyanate and the polyol are reacted with each other at a mole ratio of 1.1:1 to 4:1 to form the polyisocyanate. The polyisocyanate dispersed in water is reacted with a chain extender for post-polymerization. The suitable chain extender as used herein is polyamines, the example of which include hydrazine, ethylenediamine, piperazine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, N,N,N'-tris(2-aminoethyl)amine, N-(2-piperazinoethyl)ethylenediamine, N,N'-bis(2-aminoethyl)piperazine, N,N,N'-tris(2-aminoethyl)ethylenediamine, N-[N-(2-aminoethyl)-2-aminoethyl]-N'-(2-aminoethyl)piperazine, N-(2-aminoethyl)-N'-(2-piperazinoethyl)ethylenediamine, N,N-bis(2-aminoethyl)-N-(2-piperazinoethyl)amine, N,N-bis(2-piperazinoethyl)amine, guanidine, melamine, N-(2-aminoethyl)-1,3-propanediamine, 3,3'-diaminobenzidine, 2,4,6-triaminopyrimidine, dipropylenetriamine, tetrapropylenepentamine, tripropylenetetramine, N,N-bis(6-aminoethyl)amine, N,N'-bis(3-aminopropyl)ethylenediamine, 2,4-bis(4'-aminobenzyl)aniline, 1,4-butanediamine, 1,6-hexanediamine, 1,8-octanediamine, 1,10-decanediamine, 2-

methylpentamethylenediamine, 1,12-dodecanediamine, isophorondiamine (or 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane), and bis(4-aminocyclohexyl)methane (or bis(aminocyclohexane-4-yl)-methane).

Thus obtained is the aqueous polyurethane dispersion, which has preferably
5 a solid resin content of 20 to 50% and more preferably 20 to 30%, and a particle size of 50 to 200 nm. The aqueous polyurethane dispersions is commercially available.

The aqueous polyurethane dispersion composition for synthetic leather preferably has a viscosity of 500 to 5,000 cps and more preferably 1,000 to 3,000 cps for being used as an impregnating composition; or preferably has a viscosity of 5,000
10 to 15,000 cps and more preferably 5,000 to 10,000 cps for being used as a coating composition. For the control of the viscosity, a thickening agent commercially available, such as urethane, acryl, or cellulose-based thickening agent

The water repellent as used herein is a fluorine compound or a silicon compound, which are commercially available as well known to those skilled in the art,
15 and the specific example of the water repellent include Zonyl (e.g., 8412TM or RNTM) supplied by Ciba-Geygy Co., Scotch guard (e.g., FC255TM or FC214-230TM) supplied by 3M Co., and Teflon (e.g., 8070TM or 8787TM) supplied by Dupon Co. The water repellent enhances water repellent property and water resistance and aids formation of the cells in the synthetic leather thus obtained. If the amount of the water repellent is
20 less than 0.1 part by weight, the synthetic leather obtained has a significant deterioration of water resistance and water repellent property. An excess of the water repellent more than 5 parts by weight has undesirable effects on the synthetic leather, such as deterioration in mechanical properties, texture and appearance (e.g., greasiness).

The emulsifier as used herein is an anionic or non-ionic emulsifier and preferably selected from the group consisting of sodium bis(2-ethylhexyl)sulfosuccinate, sodium laurylsulphate, sodium isopropyl naphthalene sulfonate, sodium bis(tridecyl)sulfosuccinate, n-octadecyldisodium sulfosuccinate, 5 octylphenoxypoly(ethyleneoxy)ethanol, trimethylnonyloxypoly(ethyleneoxy)ethanol, nonylphenoxypoly(ethyleneoxy)ethanol, glyceryltriolate, ethylene glycol ethylene monostearate, sorbitanetriolate, sorbitanetristerate and mixtures thereof. The emulsifier has a function of aiding formation of cells in the coating layer in the preparation of the synthetic leather. If the amount of the emulsifier is less than 0.1 10 part by weight, the cells in the synthetic leather may crash during the drying step. With an excess of the emulsifier more than 8 parts by weight, the synthetic leather has the surface with cracks and a deterioration of the antifoaming effect when the synthetic leather being dried.

The antifoamer as used herein is a silicon-based antifoamer, preferably in 15 combination with lipophilic particles (e.g., polyurea) in order to enhance the dispersability and antifoaming characteristic of the silicon oil. An example of the suitable antifoamer is an organically modified polysiloxane, which is commercially available as well known to those skilled in the art. The antifoamer prevents the formation such as small crater on the surface of synthetic leather and controls the 20 number and size of the internal cells in the synthetic leather. Less than 0.1 part by weight of the antifoamer deteriorates the antifoaming effect and makes it hard to control the number and size of the cells in the coating layer, whereas an excess of the antifoamer more than 8 parts by weight deteriorates the mechanical properties of the complete synthetic leather and inhibits formation of cells in the synthetic leather, as a

result of which the softness of the synthetic leather is deteriorated.

The inorganic filler as used herein is a commercially available inorganic filler, the example of which is a powder of modified silica, titanium oxide, alumina, ferric oxide, calcium oxide or magnesium oxide with an average diameter of around 1 μm , and mixtures thereof. An amount of the inorganic filler less than 0.1 part by weight deteriorates the abrasion resistance and prevents formation of cells in the coating layer, whereas an excess of the inorganic filler greater than 5 parts by weight deteriorates the softness of the synthetic leather.

The aqueous polyurethane resin composition according to the present invention as obtained by mixing additives including water-repellent, emulsifier, antifoamer and inorganic filler with an aqueous polyurethane dispersion is impregnated into a substrate, mechanically foamed or defoamed and then coated on the substrate. Subsequently, the coated substrate is coagulated with a coagulating solution, which is selected from the group consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and mixtures thereof.

The mechanical foaming step is effected with a known stirring machine called "mechanical stirrer". The defoaming step is also effected with a commercially available pressure container operating under vacuum. The mechanical stirrer and the pressure container are both well known to those skilled in the art.

The impregnation prior to the coating step and the coating of the aqueous polyurethane dispersion composition on the substrate are achieved by a known method such as dipping or glazing coating (e.g., embossing coating), which is well known to those skilled in the art.

The coagulating solution as used herein is preferably selected from the group consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and mixtures thereof. Examples of the salts contained in the aqueous solution of salts as a coagulating solution include: (a) all general salts including sodium chloride (NaCl), silver chloride (AgCl), silver bromide (AgBr), silver iodide (AgI), silver chromate (AgCrO₄), barium carbonate (BaCO₃), barium fluoride (BaF₂), calcium carbonate (CaCO₃), mercury chloride (PbCl₂), magnesium carbonate (MgCO₃), lead chloride (PbCl₂), silver nitrate (AgNO₃), copper sulfate (CuSO₄), copper chloride (CuCl₂), and lead sulfate (PbSO₄); (b) sodium chloride, potassium chloride, calcium chloride, sodium sulfate and calcium sulfate, which are obtained by neutralization between a strong acid (e.g., hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, hydrogen bromide, hydrogen iodide, nitrous acid, hypochlorous acid, etc.) and a strong base (e.g., sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, ammonia, etc.); (c) ammonium chloride, ammonium sulfate, ammonium bromide and sodium carbonate, which are obtained by neutralization between a strong acid as defined above and a weak base including almost all water soluble amines; (d) CH₃COONa, CH₃CH₂COONa, CH₃COOK and C₆H₅Na, which are obtained by neutralization between a strong base as defined above and a weak acid (e.g., fluoric acid, hydrogen sulfide, carbonic acid, sodium carbonate, carboxylic acids such as CH₃COOH and CH₃CH₂COOH; and (e) CH₃COONH₄ and CH₃CH₂COONH₄, which are obtained by neutralization between a weak acid and a weak base as defined above. The coagulating solution may have a pH value variable depending on the type and amount of the salt used therein and preferably controlled

in the range from 3 to 11. The pH value of the coagulating solution can be controlled by adding an acid or base to the aqueous solution of the salt, or regulating the equivalent weight of the acid and base used in the preparation of the aqueous solution of the salt.

- 5 The temperature of the coagulating solution in the coagulation bath is preferably in the range of 10 to 50 °C.

Following the coagulation step, the substrate is subjected to a post-treatment including washing, drying, embossing, buffing and weight reducing to produce the complete synthetic leather, the post-treatment method being well known to those
10 skilled in the art.

The method for preparing a synthetic leather from an aqueous polyurethane dispersion according to the present invention includes the steps of: (a) preparing a coating composition comprising 100 parts by weight of an aqueous polyurethane dispersion, 0.1 to 5 parts by weight of a water repellent, 0.1 to 8 parts by weight of an
15 emulsifier, 0.1 to 1 part by weight of an antifoamer, and 0.1 to 5 parts by weight of an inorganic filler, and subjecting the coating composition to mechanical foaming or defoaming, wherein aqueous polyurethane dispersion is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group; (b) impregnating the aqueous polyurethane dispersion
20 composition into a substrate including a woven or nonwoven fabric; (c) coating the substrate obtained in step (b) with the polyurethane dispersion foamed or defoamed in step (a); (d) coagulating the coated substrate with a coagulating solution selected from the group consisting of an aqueous solution of various salts, a mixed solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and

mixtures thereof; and (e) subjecting the coagulated substrate to a post-treatment including washing, and drying, etc.

5 In the step (a) of preparing the coating composition, the above-described aqueous polyurethane dispersion is mixed with additives such as water repellent, emulsifier, antifoamer and inorganic filler and the mixture is subjected to a mechanical foaming or defoaming step. The foamed or defoamed coating composition is applied to the substrate taken immediately after step (b) by a known coating method and passed through a coagulation bath containing the coagulating solution in the subsequent coagulation step, allowing the polyurethane dispersion to
10 be coagulated into a synthetic leather. The thickness of the coating is in the range of 0.1 to 3 mm. If the thickness of the coating is less than 0.1 mm, the leather layer of the synthetic leather is too thin to provide the properties peculiar to the leather. On the other hand, the thickness of coating greater than 3 mm deteriorates the properties of the synthetic leather.

15 In the step (b) of preparing the substrate, the aqueous polyurethane dispersion is mixed with additives such as water repellent, emulsifier, antifoamer and inorganic filler, and the mixture is thickened with a thickening agent to have a viscosity of 500 to 5,000 cps and preferably 1,000 to 3,000 cps. The mixture is then impregnated into a woven or nonwoven fabric, which is applied to the subsequent coating step. The
20 impregnation rate is in the range of 5 to 90% and preferably 5 to 50% based on the total weight of the woven or nonwoven fabric. An impregnation rate of less than 5% deteriorates the mechanical properties of the synthetic leather including tensile strength and abrasion resistance, whereas an impregnation rate exceeding 90% deteriorates the softness of the synthetic leather.

According to the present invention, the coagulation step (d) controls the shape, size and density of cells depending on the type, pH value and concentration of the aqueous solution of the salt to prevent formation such as small craters on the surface, which allows production of a synthetic leather with good properties such as coating property.

The coagulating solution can be an aqueous solution of any general salt including silver chloride, silver bromide, silver iodide, silver chromate, barium carbonate, barium fluoride, calcium carbonate, mercury chloride, magnesium carbonate, lead chloride, silver nitrate, copper sulfate, copper chloride and lead sulfate.

The coagulating solution can also be an aqueous solution of salts including sodium chloride, potassium chloride, calcium chloride, sodium sulfate and calcium sulfate, which are obtained by neutralization between a strong acid (e.g., hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, hydrogen bromide, hydrogen iodide, nitrous acid, hypochlorous acid, etc.) and a strong base (e.g., sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, ammonia, etc.).

The coagulating solution can also be an aqueous solution of salts including ammonium chloride, ammonium sulfate, ammonium bromide and sodium carbonate, which are obtained by neutralization between a strong acid (e.g., hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, hydrogen bromide, hydrogen iodide, nitrous acid, hypochlorous acid, etc.) and a weak base including almost all water soluble amines.

The coagulating solution can also be an aqueous solution of salts including CH_3COONa , $\text{CH}_3\text{CH}_2\text{COONa}$, CH_3COOK and $\text{C}_6\text{H}_5\text{Na}$, which are obtained by

neutralization between a strong base (e.g., sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, ammonia, etc.) and a weak acid (e.g., fluoric acid, hydrogen sulfide, carbonic acid, sodium carbonate, carboxylic acids such as CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$).

5 The coagulating solution can also be an aqueous solution of salts including $\text{CH}_3\text{COONH}_4$ and $\text{CH}_3\text{CH}_2\text{COONH}_4$, which are obtained by neutralization between a weak acid (e.g., fluoric acid, hydrogen sulfide, carbonic acid, sodium carbonate, carboxylic acids such as CH_3COOH and $\text{CH}_3\text{CH}_2\text{COOH}$ and a weak base including almost all water soluble amines.

10 Besides, the coagulating solution can be a mixed aqueous solution obtained by adding an acid or base to the aqueous solution of the salt, or regulating the equivalent weight of the acid and base used in the preparation of the aqueous solution of the salt.

 In the coagulation step (d), the salt content in the coagulating solution is preferably in the range of 5 to 50 wt.% and more preferably in the range of 20 to 40
15 wt.%. The salt content of less than 5 wt.% causes the cells crashed during the drying step, whereas the salt content of greater than 50 wt.% involves a problem in the washing step. In controlling the pH value of the coagulating solution with an addition of an acid or base to the aqueous solution of the salt, the pH value is preferably in the range of 3 to 11 and more preferably in the range of 4 to 10. For example, the pH
20 value of the coagulating solution is in the range of 3 to 7 for an anionic polyurethane dispersion and 7 to 11 for a cationic polyurethane dispersion. If the pH value of the coagulating solution is less than 3 for the anionic polyurethane dispersion or greater than 11 for the cationic polyurethane dispersion, the cells are scarcely formed in the synthetic leather.

Hereinafter, the present invention will be described in detail by way of the following examples, which are not intended to limit the scope of the present invention.

Example 1

A coating composition and an impregnating composition were prepared at the composition ratio shown in Tables 1 and 2.

Table 1

Material	Parts by weight
Aqueous polyurethane dispersion	100
Thickening agent (Acrysol RM-825 from Rohm & Hass Inc.)	3
Antifoamer (BYK-022 from BYK-chemy Inc.)	0.3
Inorganic filler (Nipsil E-170 from Nippon Silica Inc.)	0.15
Water repellent (Neosilk SDB from Daedong Inc.)	3
Emulsifier (ammonium stearate)	0.2

* Aqueous polyurethane dispersion is available from Nanopol Inc., in Korea by the trade name NPL-5000(solid contents 25% by weight, ion contents 3.5%/solid by weight, anionic polyurethane emulsion).

Table 2

Material	Parts by weight
Aqueous polyurethane dispersion*	100
Thickening agent (Acrysol RM-825 from Rohm & Hass Inc.)	0.2
Antifoamer (BYK-024 from BYK-chemy Inc.)	0.2
Inorganic filler (Nipsil E-170 from Nippon Silica Inc.)	0.05
Water repellent (Neosilk SDB from Daedong Inc.)	5
Emulsifier (ammonium stearate)	0.1

* Aqueous polyurethane dispersion is available from Nanopol Inc., in Korea by the trade name NPL-5200(solid contents 25% by weight, ion contents 1.8%/solid by weight, anionic polyurethane emulsion).

5

The coating composition prepared according to Table 1 was defoamed with a pressure container and coated on a nonwoven fabric which was previously dipped in the impregnating composition as prepared according to Table 2, using a glazing coating for an embossing process. The coated nonwoven fabric was immersed in a

10 coagulation bath containing a coagulating solution for 5 minutes. Here, the coagulating solution was obtained by adding ammonia (NH_3) to 30 wt.% of an aqueous solution of phosphoric acid and controlled to have a pH value of 4. Removed from the coagulation bath, the coated nonwoven fabric was washed and dried to obtain a synthetic leather. FIG. 1 presents a microscopic photograph showing an enlarged cross section of the

15 synthetic leather. As is apparent from FIG. 1, numerous closed cells are uniformly

provided in the synthetic leather and the surface of the synthetic leather become smooth.

Example 2

A coating composition was prepared at the composition ratio shown in Table

5 3.

Table 3

Material	Parts by weight
Aqueous polyurethane dispersion*	100
Thickening agent (Acrysol RM-825 from Rohm & Hass Inc.)	3
Antifoamer (BYK-022 from BYK-chemy Inc.)	0.1
Inorganic filler (Nipsil HD from Nippon Silica Inc.)	0.15
Water repellent (Versilk from Daedong Inc.)	3
Emulsifier (ammonium stearate)	0.2

* Aqueous polyurethane dispersion is available from Nanopol Inc., in Korea by the trade name NPL-5100(solid contents 25% by weight, ion contents 2.5%/solid by weight, anionic polyurethane emulsion).

10

The coating composition prepared according to Table 3 was foamed with a foamer to have uniform open cells and coated on a nonwoven fabric which was dipped in the impregnating composition prepared in Example 1. The coated nonwoven fabric was immersed in a coagulation bath containing a coagulating solution for 5 minutes. Here, the coagulating solution was obtained by adding

15

ammonia (NH_3) to 30 wt.% of an aqueous solution of phosphoric acid and controlled to have a pH value of 4. Removed from the coagulation bath, the coated nonwoven fabric was washed and dried to obtain a synthetic leather. FIG. 2 presents a microscopic photograph showing an enlarged cross section of the synthetic leather.

As is apparent from FIG. 2, numerous closed cells are uniformly provided in the synthetic leather and the surface of the synthetic leather become smooth.

Example 3

An impregnating composition was prepared at the composition ratio shown in Table 4.

Table 4

Material	Parts by weight
Aqueous polyurethane dispersion*	100
Thickening agent (Acrysol RM-825 from Rohm & Hass Inc.)	0.2
Antifoamer (BYK-022 from BYK-chemy Inc.)	0.2
Inorganic filler (Nipsil HD from Nippon Silica Inc.)	0.15
Water repellent (Versilk from Daedong Inc.)	5
Emulsifier (ammonium stearate)	0.2

* Aqueous polyurethane dispersion is available from Nanopol Inc., in Korea by the trade name NPL-5300 (solid contents 25% by weight, ion contents 2%/solid by weight, anionic polyurethane emulsion).

The impregnating composition prepared according to Table 4 was impregnated into a superfine nonwoven fabric for suede-like synthetic leather without a coating step, and the impregnated nonwoven fabric was heated and passed between pressure rollers to provide an impregnation rate of 45% with respect to the nonwoven
5 fabric. The impregnated nonwoven fabric was immersed in a coagulation bath containing a coagulating solution for 5 minutes. Here, the coagulating solution was obtained by adding ammonia (NH_3) to 30 wt.% of an aqueous solution of phosphoric acid and controlled to have a pH value of 4. Removed from the coagulation bath, the coated nonwoven fabric was washed and dried to obtain a synthetic leather. FIG. 3
10 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As is apparent from FIG. 3, the polyurethane resin is uniformly distributed over the nonwoven fabric other than the surface and has a space from the fiber unit to provide sufficient softness and bulkiness to the suede-like synthetic leather for suede.

Example 4

15 The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 10 wt.% of an aqueous solution of sodium chloride was used as a coagulating solution. FIG. 4 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As shown in
FIG. 4, the use of sodium chloride in the coagulating solution caused an increase in
20 formation of the cell-free region.

Example 5

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 20 wt.% of an aqueous solution of sodium chloride was used as a coagulating solution. FIG. 5 presents a microscopic

photograph showing an enlarged cross section of the synthetic leather. As shown in FIG. 5, an increased concentration of the aqueous sodium chloride solution used as a coagulating solution caused an increase in formation of the cell-free region.

Example 6

7 A coating composition and an impregnating composition were prepared at the composition ratio shown in Tables 5 and 6.

Table 5

Material	Parts by weight
Aqueous polyurethane dispersion	100
Thickening agent (Acrysol RM-825 from Rohm & Hass Inc.)	3
Antifoamer (BYK-022 from BYK-chemy Inc.)	0.3
Inorganic filler (Nipsil E-170 from Nippon Silica Inc.)	0.15
Water repellent (Neosilk SDB from Daedong Inc.)	3

* Aqueous polyurethane dispersion is a cationic polyurethane emulsion
10 having solid contents 25% by weight and ion contents 10%/solid by weight.

Table 6

Material	Parts by weight
Aqueous polyurethane dispersion*	100
Thickening agent (Acrysol RM-825 from Rohm & Hass Inc.)	0.2
Antifoamer (BYK-024 from BYK-chemy Inc.)	0.2
Inorganic filler (Nipsil E-170 from Nippon Silica Inc.)	0.05
Water repellent (Neosilk SDB from Daedong Inc.)	5

* Aqueous polyurethane dispersion is a cationic polyurethane emulsion having solid contents 25% by weight and ion contents 10%/solid by weight.

5 The coating composition prepared according to Table 5 was defoamed with a defoamer and coated on a nonwoven fabric which was previously dipped in the impregnating composition as prepared according to Table 6. using a glazing coating for an embossing process. The coated nonwoven fabric was immersed in a coagulation bath containing a coagulating solution for 5 minutes. Here, the

10 coagulating solution was obtained by mixing a 20% aqueous mixed solution of nitric acid with potassium hydroxide at the mole ratio of 1:1. Removed from the coagulation bath, the coated nonwoven fabric was washed and dried to obtain a synthetic leather. FIG. 6 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As is apparent from FIG. 6, the cationic

15 polyurethane resin emulsion is also coagulated by the action of salt to produce the synthetic leather.

Example 7

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 6 excepting that a 30% aqueous mixed solution of nitric acid and potassium hydroxide at the mole ratio of 1:1 was used as a coagulating solution. FIG. 7 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As shown in FIG. 7, an increased concentration of the aqueous solution of the salt reduced the number of porous cells to almost zero.

Example 8

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that a 20% aqueous mixed solution of nitric acid and ammonia at the mole ratio of 1:1 was used as a coagulating solution. FIG. 8 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As shown in FIG. 8, the cells had a more apparent cylindrical form relative to those of Example 1. That is, the shape of the cells can be varied depending on the type of the salt used in the coagulating solution.

Example 9

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that a 30% aqueous mixed solution of nitric acid and ammonia at the mole ratio of 1:1 was used as a coagulating solution. FIG. 9 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As shown in FIG. 9, an increased content of the salt in the coagulation solution allowed a production of the cell-free synthetic leather. This demonstrates that the content of the salt is an important factor in controlling the shape of the cells.

Example 10

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that a 20% aqueous mixed solution of phosphoric acid and potassium hydroxide at the mole ratio of 1:1 was used as a coagulating solution. FIG. 10 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. Compared to Example 1, this example used potassium hydroxide as a base in phosphoric acid instead of ammonia and showed that the shape of the cells can be varied depending on the type of the salt. The use of potassium hydroxide entirely reduced the uniformity of the cells but increased the size of the cells.

Example 11

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that a 30% aqueous mixed solution of phosphoric acid and potassium hydroxide at the mole ratio of 1:1 was used as a coagulating solution. FIG. 11 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. As shown in FIG. 11, an increased content of the salt in the coagulating solution caused an increase in formation of the cell-free region.

Example 12

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that a 20% aqueous mixed solution of phosphoric acid and tributylamine at the mole ratio of 1:1 was used as a coagulating solution. FIG. 12 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. Compared to Example 1, this example used

tributylamine as a base in phosphoric acid instead of ammonia and showed that the shape of the cells can be varied depending on the type of the salt. The use of tributylamine entirely reduced the uniformity of the cells but increased the size of the cells.

5 **Example 13**

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that a 30% aqueous mixed solution of phosphoric acid and tributylamine at the mole ratio of 1:1 was used as a coagulating solution. FIG. 13 presents a microscopic photograph showing an enlarged cross
10 section of the synthetic leather. As shown in FIG. 13, an increased content of the salt in the coagulating solution caused an increase in formation of a cell-free region and reduced the thickness of the surface coating.

Example 14

The procedures were performed to obtain a synthetic leather in the same
15 manner as described in Example 1 excepting that 10 wt.% of an aqueous sodium chloride solution was mixed with 30 wt.% of aqueous phosphoric acid solution to provide a coagulating solution having a controlled pH value of 5. FIG. 14 presents a microscopic photograph showing an enlarged cross section of the synthetic leather.

Example 15

20 The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 20 wt.% of an aqueous sodium chloride solution was mixed with 30 wt.% of aqueous phosphoric acid solution to provide a coagulating solution having a controlled pH value of 5. FIG. 15 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. In

regard to Examples 14 and 15, a decreased pH value of the coagulating solution, i.e., acidification caused an increase in formation of the cell-free synthetic leather.

Example 16

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 10 wt.% of an aqueous sodium chloride solution was mixed with 30 wt.% of aqueous potassium hydroxide solution to provide a coagulating solution having a controlled pH value of 10. FIG. 16 presents a microscopic photograph showing an enlarged cross section of the synthetic leather.

Example 17

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 20 wt.% of an aqueous sodium chloride solution was mixed with 30 wt.% of aqueous potassium hydroxide solution to provide a coagulating solution having a controlled pH value of 10. FIG. 17 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. In regard to Examples 16 and 17, an increased pH value of the coagulating solution, i.e., alkalization caused a sharp increase in the size of the cells.

Example 18

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 20 wt.% of an aqueous phosphoric acid solution was mixed with ammonia to provide a coagulating solution having a controlled pH value of 4. FIG. 18 presents a microscopic photograph showing an enlarged cross section of the synthetic leather.

Example 19

The procedures were performed to obtain a synthetic leather in the same manner as described in Example 1 excepting that 30 wt.% of an aqueous phosphoric acid solution was mixed with ammonia to provide a coagulating solution having a controlled pH value of 4. FIG. 19 presents a microscopic photograph showing an enlarged cross section of the synthetic leather. In regard to Examples 18 and 19, the use of a mixed solution of acid and base instead of the solution of salt also provided numerous and uniform cells as in Example 1.

As described in the preceding examples, the present invention provides a synthetic leathers prepared in various forms. That is, as shown in FIGS. 1 and 2, the synthetic leather is internally provided with closed cells of which the size and distribution are uniformly controllable, and thus feels smooth with good texture. It is also shown in FIG. 3 that the present invention provides a suede-like synthetic leather with sufficient softness and bulkiness in which the polyurethane resin is uniformly distributed all over the nonwoven fabric other than the surface layer. As is apparent from FIGS. 4 to 11, the use of various coagulating solutions allows a control of the shape, size and density of cells and thereby effectively provides a synthetic leather of various qualities. According to these figures, the synthetic leather may have large-diameter cells with a very low density as well as those having a very small size. The density and size of the cells have an effect mainly on the texture and softness of the synthetic leather obtained so that the present invention provides a synthetic leather of various properties and makes it possible to prepare a synthetic leather of desired properties.

Consequently, the present invention provides a environment-friendly method

for preparing a synthetic leather with excellent properties and high productivity, and a synthetic leather obtained thereby. The invention also provides a method for effectively preparing a synthetic leather of various qualities in which the shape, size and density of cells are controllable depending on the coagulating solution.

5 It is to be noted that like reference numerals denote the same components in the drawings, and a detailed description of generally known function and structure of the present invention will be avoided lest it should obscure the subject matter of the present invention.

WHAT IS CLAIMED IS:

1. An aqueous type polyurethane dispersion composition for a synthetic leather, comprising:
 - 5 100 parts by weight of an aqueous polyurethane dispersion obtained from a polyurethane of which the main chain is covalently bonded to anionic groups including a carboxyl group or a sulfonate group, or cationic groups including a tertiary amine group;
0.1 to 5 parts by weight of a water repellent;
 - 10 0.1 to 8 parts by weight of an emulsifier;
0.1 to 1 part by weight of an antifoamer; and
0.1 to 5 parts by weight of an inorganic filler.
2. An aqueous polyurethane-based synthetic leather being characterized in that
 - 15 the synthetic leather is obtained by impregnating a composition comprising 100 parts by weight of aqueous polyurethane dispersion, 0.1 to 5 parts by weight of a water repellent, 0.1 to 8 parts by weight of an emulsifier, 0.1 to 1 part by weight of an antifoamer, and 0.1 to 5 parts by weight of an inorganic filler into a substrate, coating the foamed or defoamed composition on the
 - 20 substrate, and coagulating the coated substrate with a coagulating solution, wherein aqueous polyurethane dispersion is covalently bonded to anionic groups including carboxyl group or sulfonate group, or cationic groups including a tertiary amine group, wherein the coagulating solution is selected from the group consisting of an aqueous solution of various salts, a mixed

solution of salt and acid, a mixed solution of salt and base, a mixed solution of acid and base, and mixtures thereof.

3. The aqueous polyurethane-based synthetic leather as claimed in claim 2,
5 wherein the water repellent is a fluorine or a silicone compound.
4. The aqueous polyurethane-based synthetic leather as claimed in claim 2,
wherein the emulsifier is selected from the group consisting of sodium bis(2-
methylhexyl)sulfosuccinate, sodium laurylsulphate, sodium isopropyl
10 naphthalene sulfonate, sodium bis(tridecyl)sulfosuccinate, n-
octadecyldisodium sulfosuccinate, octylphenoxypoly(ethyleneoxy)ethanol,
trimethylnonyloxypoly(ethyleneoxy)ethanol,
nonylphenoxypoly(ethyleneoxy)ethanol, glyceryltriolate, ethylene glycol
ethylene monostearate, sorbitanetriolate, sorbitanetristerate and
15 mixtures thereof.
5. The aqueous polyurethane-based synthetic leather as claimed in claim 2,
wherein the antifoamer is a silicon -based antifoamer.
- 20 6. The aqueous polyurethane-based synthetic leather as claimed in claim 2,
wherein the inorganic filler is a powder selected from the group consisting of
powders of modified silica, titanium oxide, alumina, ferric oxide, calcium
oxide or magnesium oxide with an average diameter of around 1 μm , and
mixtures thereof.

7. The aqueous polyurethane-based synthetic leather as claimed in claim 2,
wherein the coagulating solution is selected from the group consisting of an
aqueous solution of various salts, a mixed solution of salt and acid, a mixed
5 solution of salt and base, a mixed solution of acid and base, and mixtures
thereof.
8. A method for preparing a synthetic leather from an aqueous polyurethane
dispersion, comprising the steps of:
- 10 (a) preparing a coating composition comprising 100 parts by weight of an
aqueous polyurethane dispersion, 0.1 to 5 parts by weight of a water repellent,
0.1 to 8 parts by weight of an emulsifier, 0.1 to 1 part by weight of an
antifoamer, and 0.1 to 5 parts by weight of an inorganic filler, and subjecting
the coating composition to mechanical foaming or defoaming, wherein the
15 aqueous polyurethane dispersion being covalently bonded to anionic groups
including carboxyl group or sulfonate group, or cationic groups including a
tertiary amine group:
- (b) impregnating the aqueous polyurethane dispersion composition into a
substrate including a woven or nonwoven fabric:
- 20 (c) coating the substrate obtained in step (b) with the aqueous polyurethane
dispersion composition foamed or defoamed in step (a):
- (d) coagulating the coated substrate with a coagulating solution selected from
the group consisting of an aqueous solution of various salts, a mixed solution
of salt and acid, a mixed solution of salt and base, a mixed solution of acid and

base, and mixtures thereof; and

(e) subjecting the coagulated substrate to a post-treatment including washing.

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FIG. 1

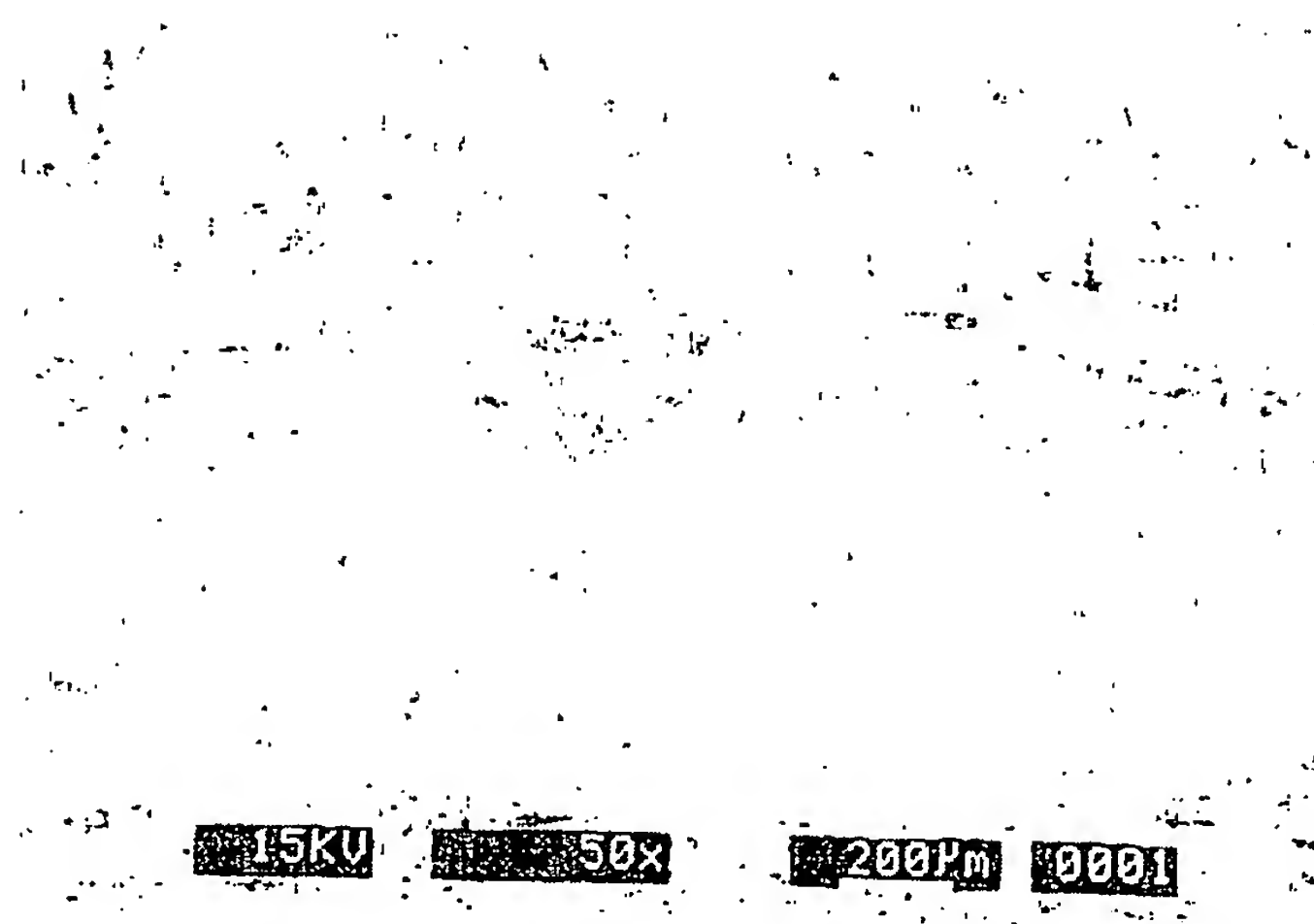


FIG. 2

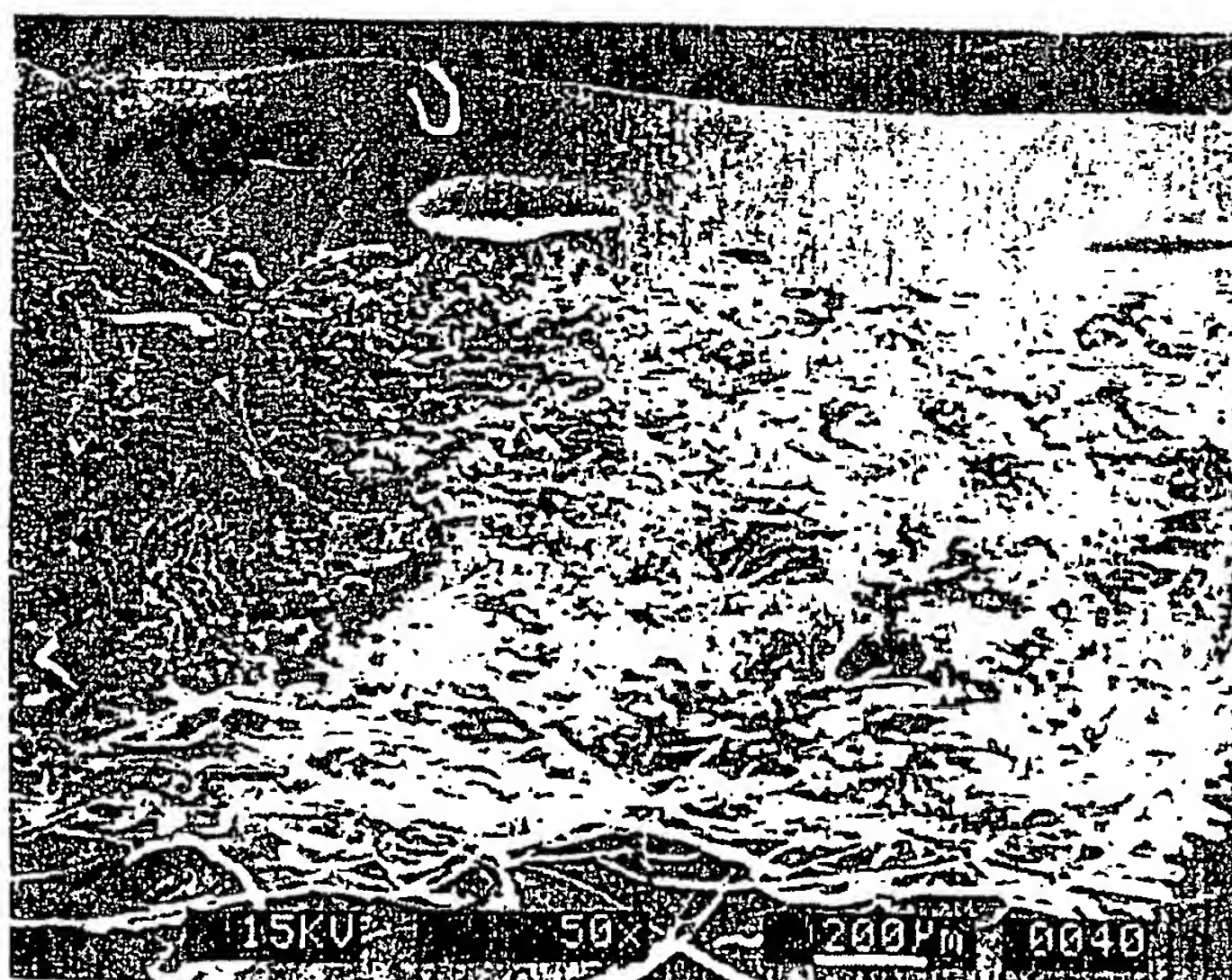


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FIG. 3



FIG. 4

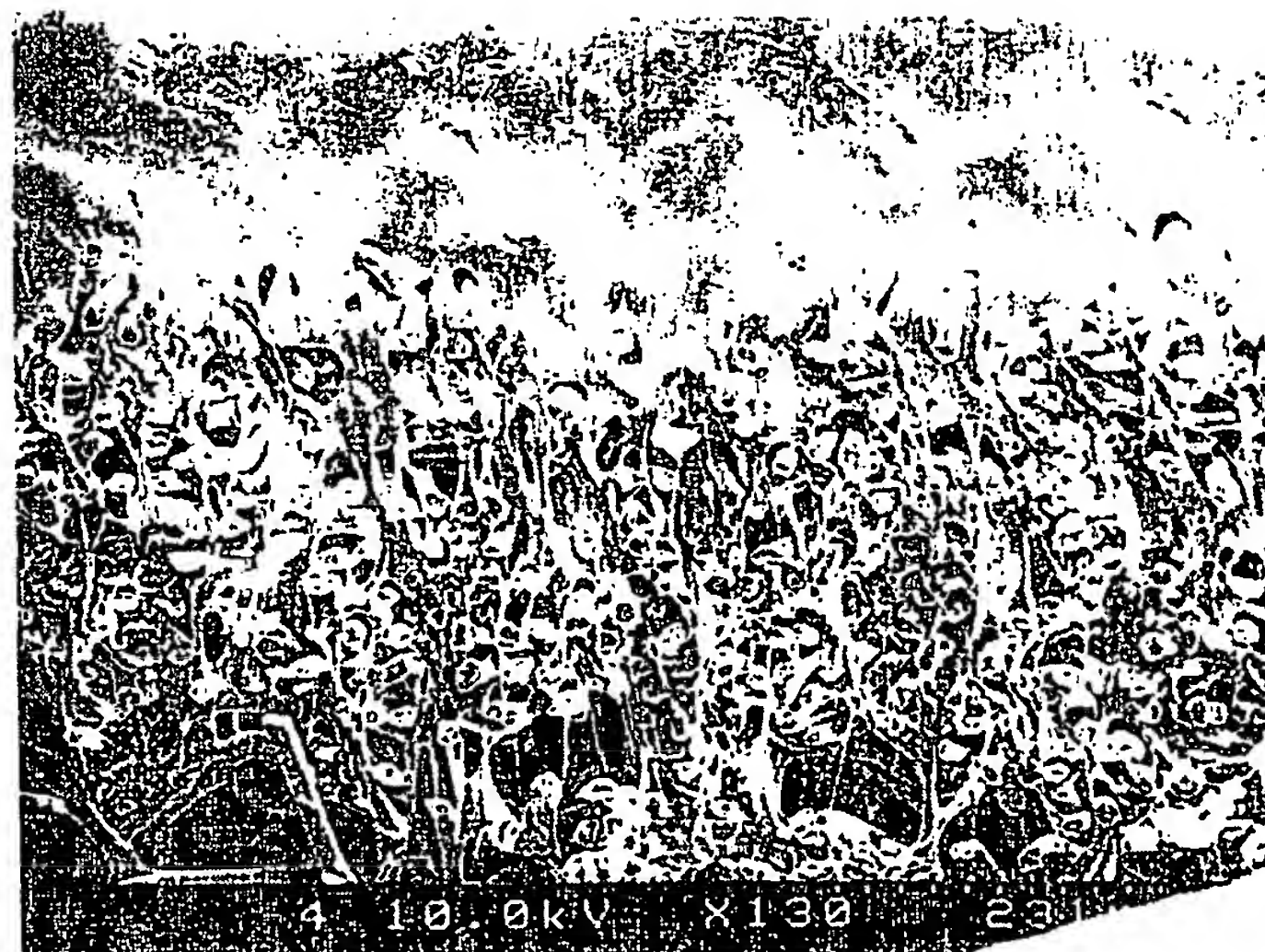


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FIG. 5



FIG. 6



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FIG. 7

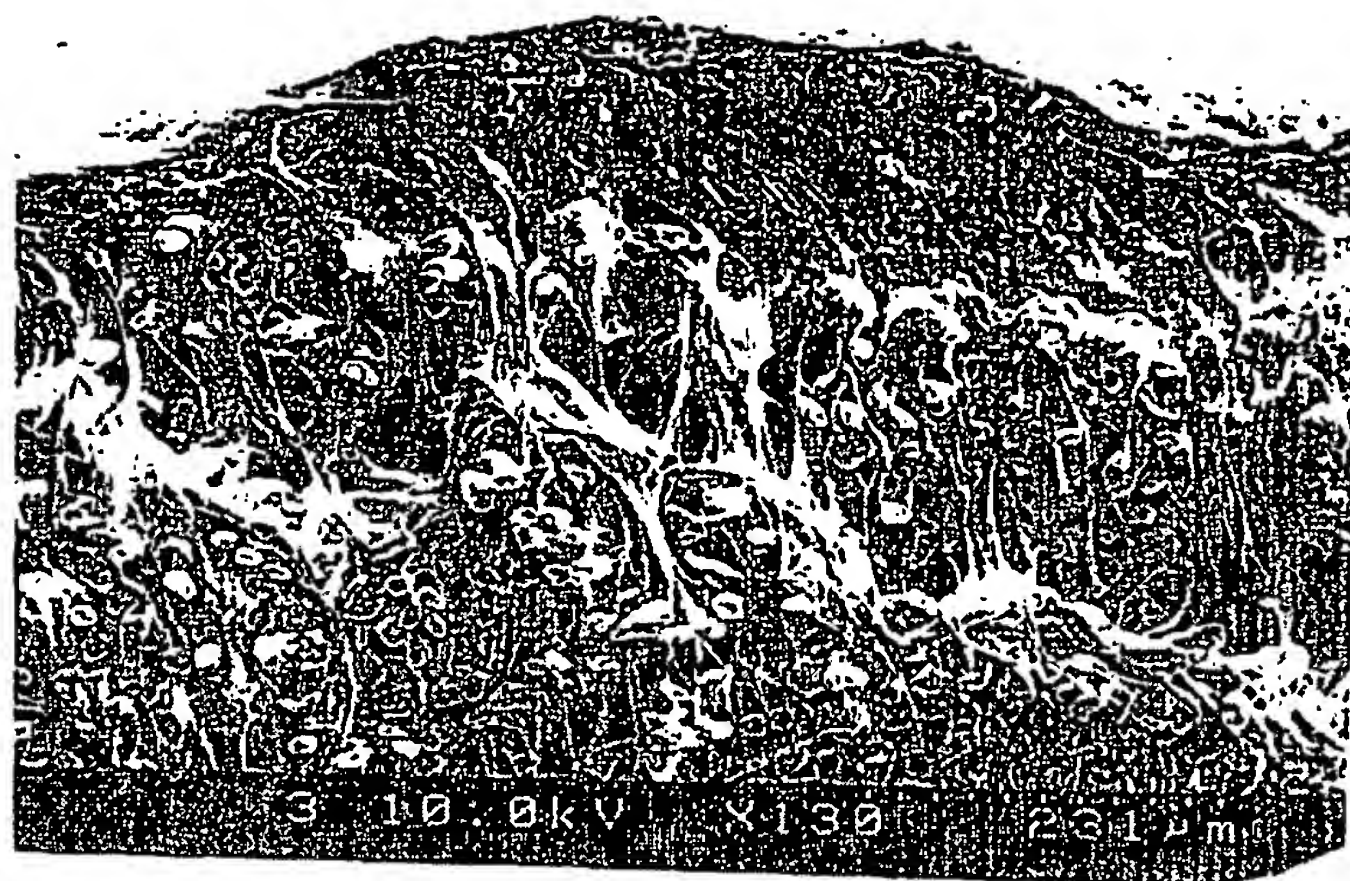


FIG. 8



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FIG. 9

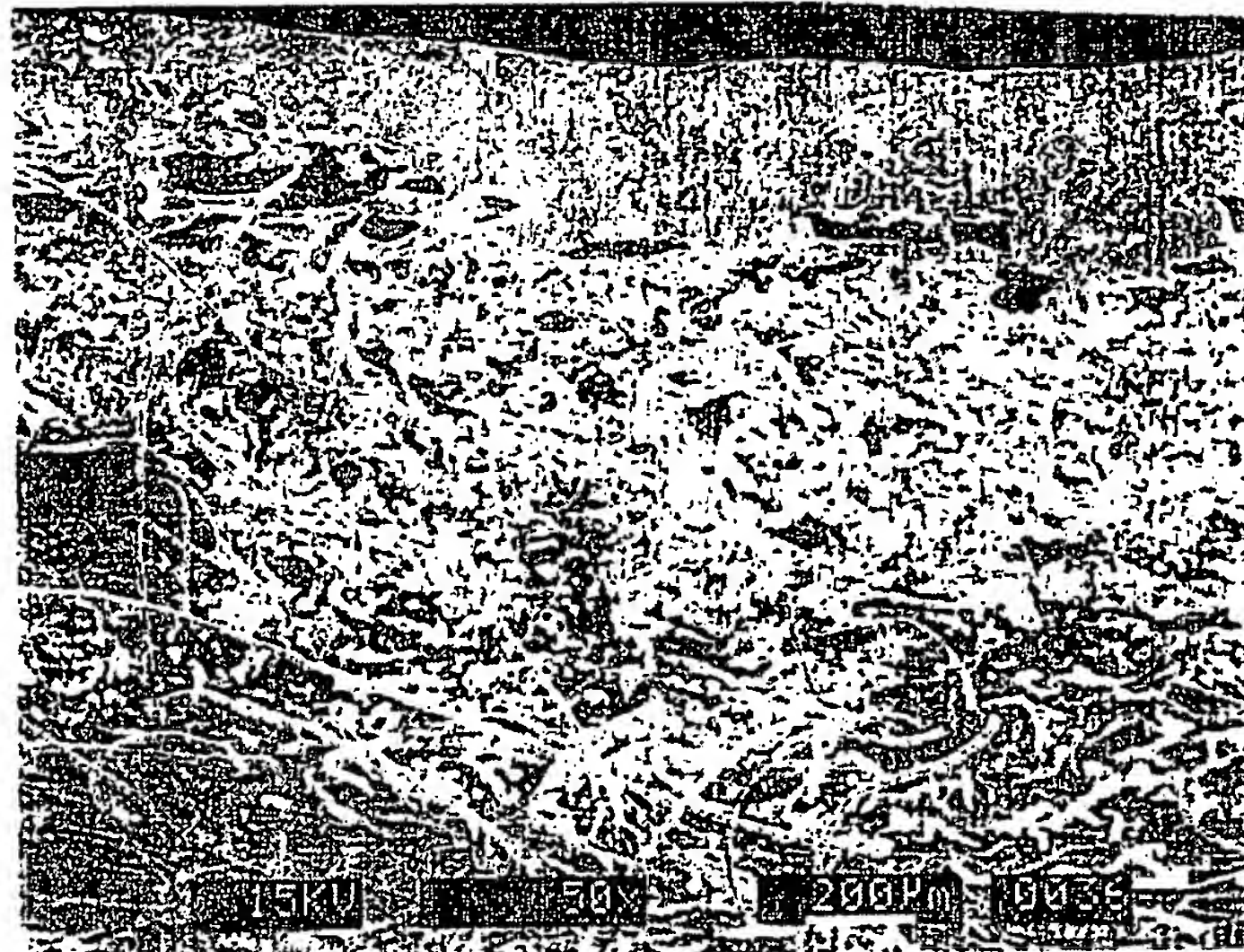
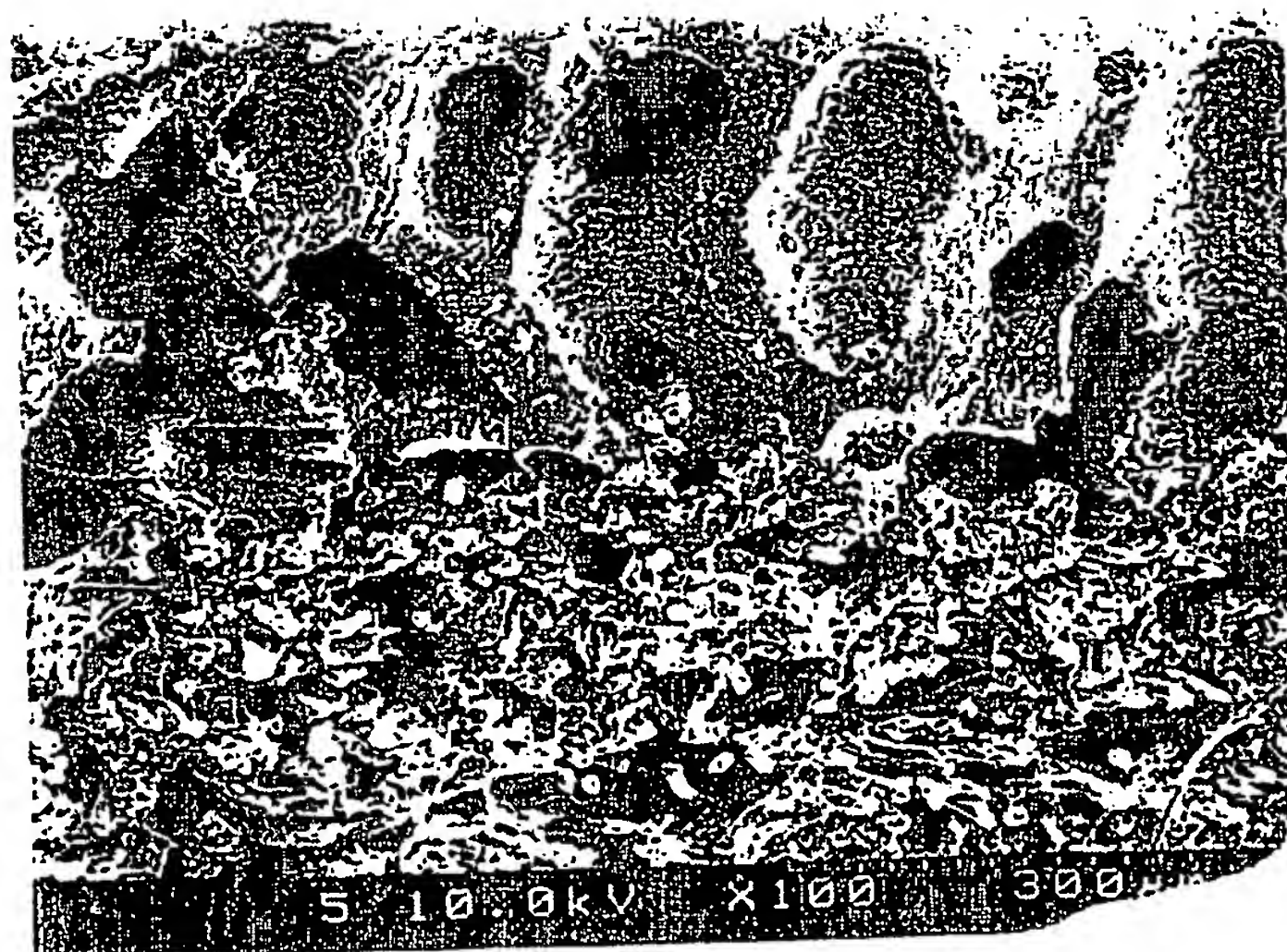


FIG. 10



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FIG. 11

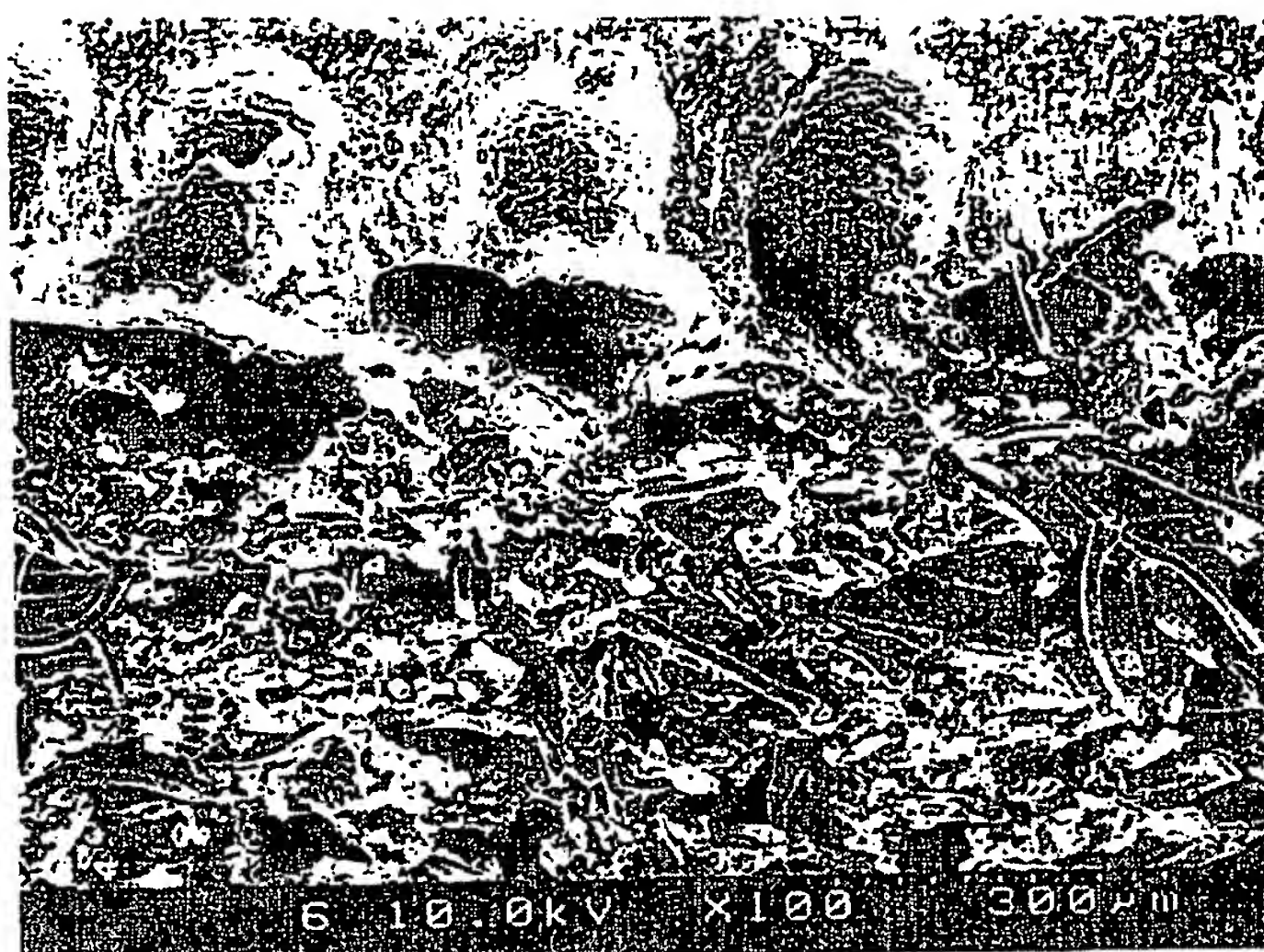
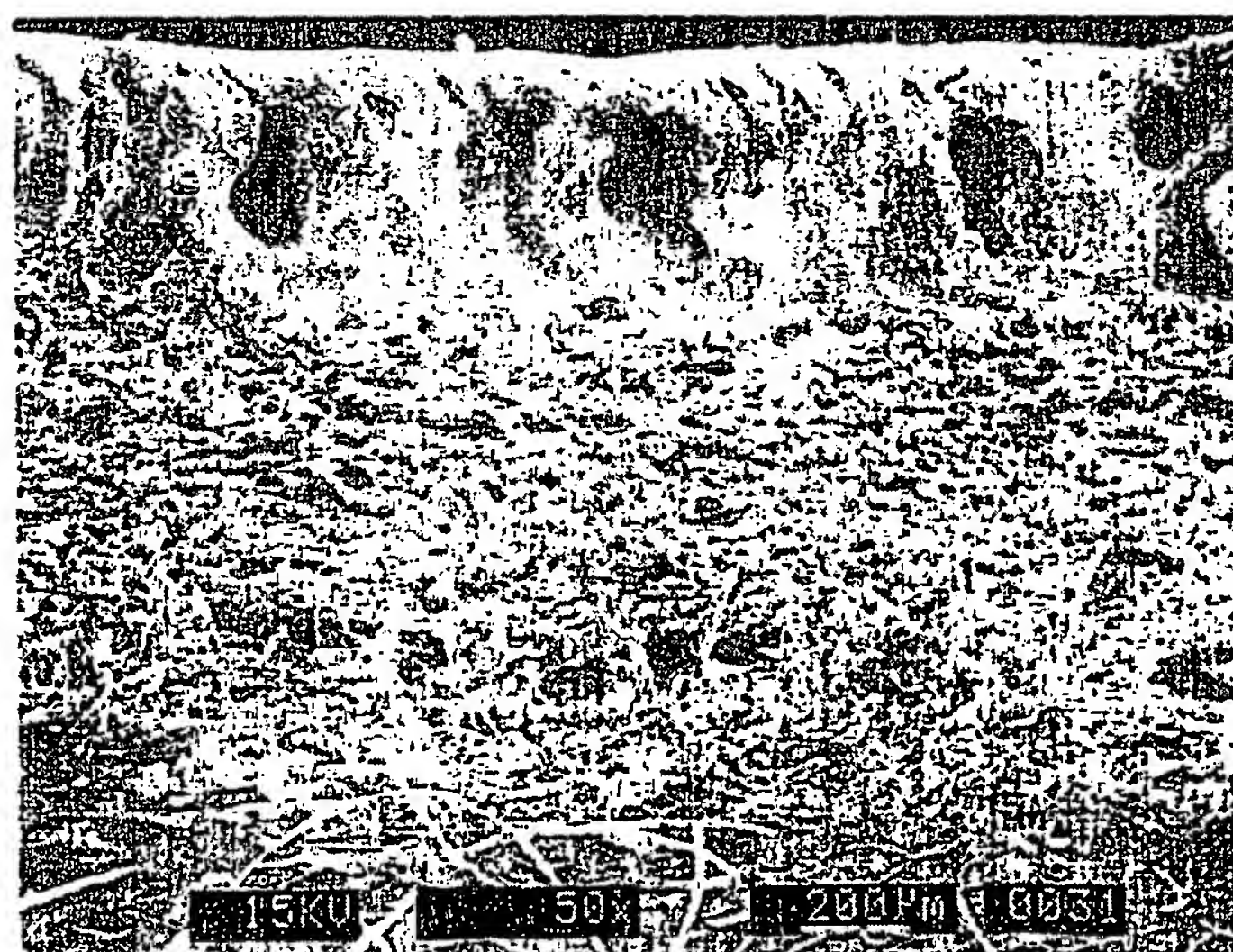


FIG. 12

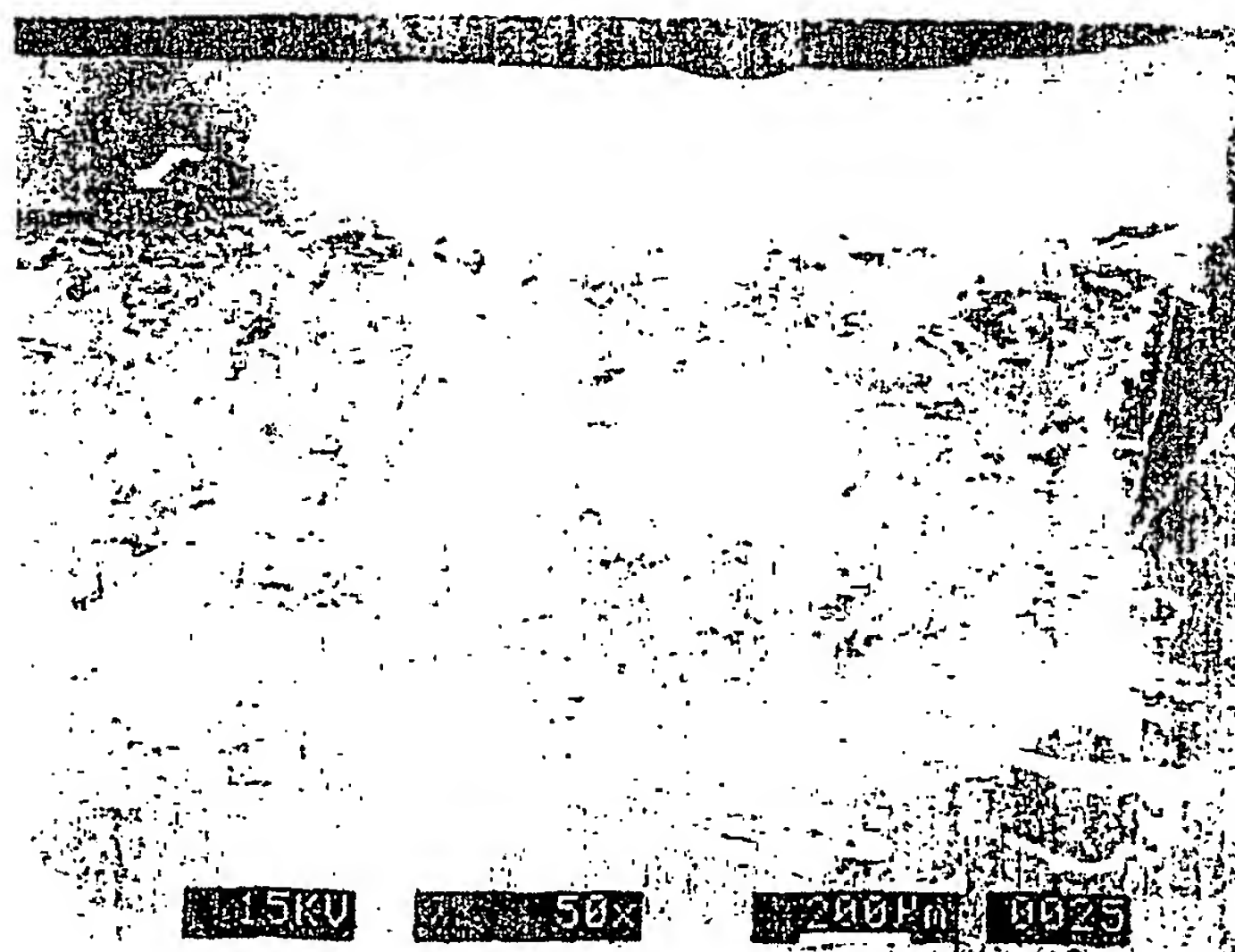


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FIG. 13



FIG. 14

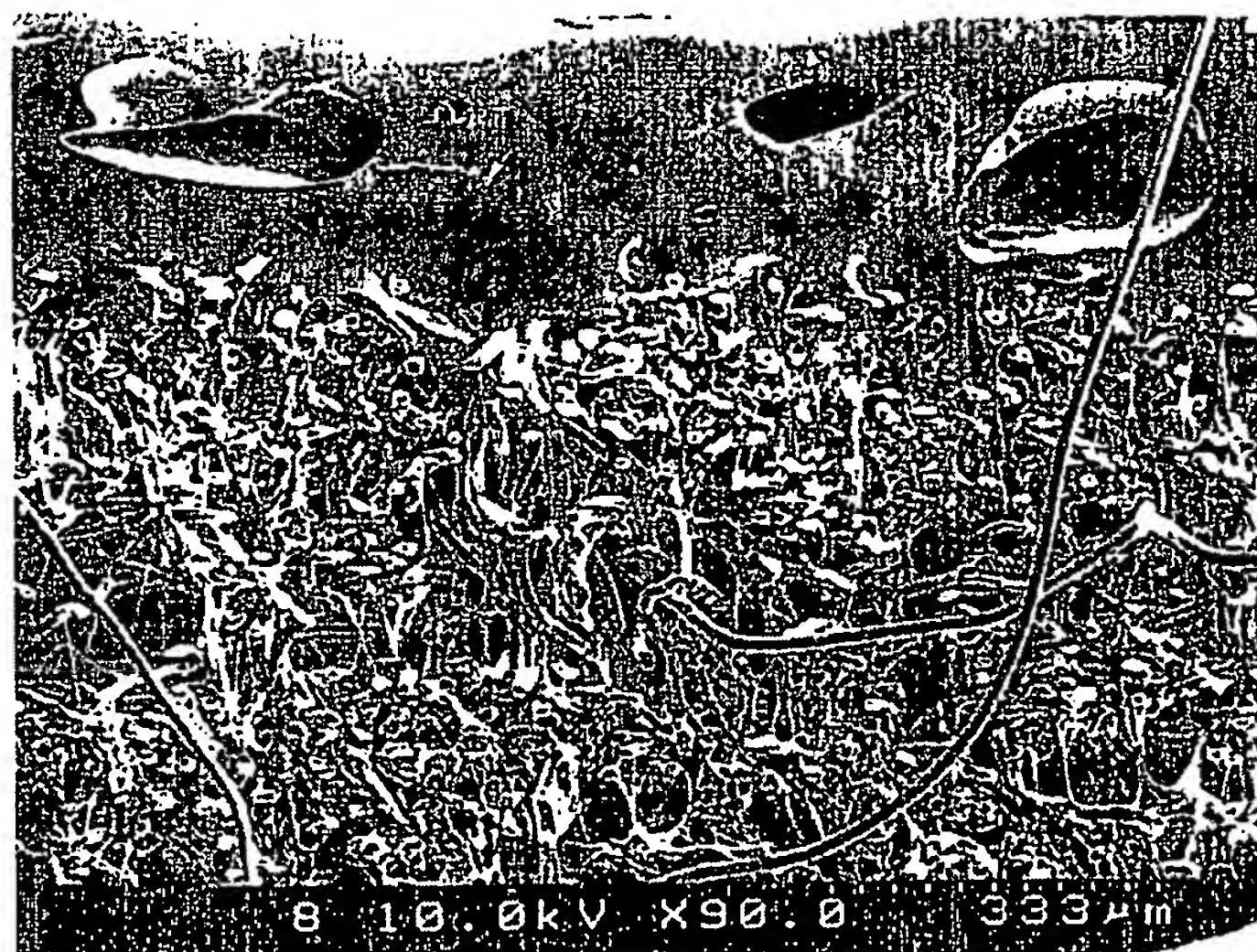


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FIG. 15



FIG. 16



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FIG. 17

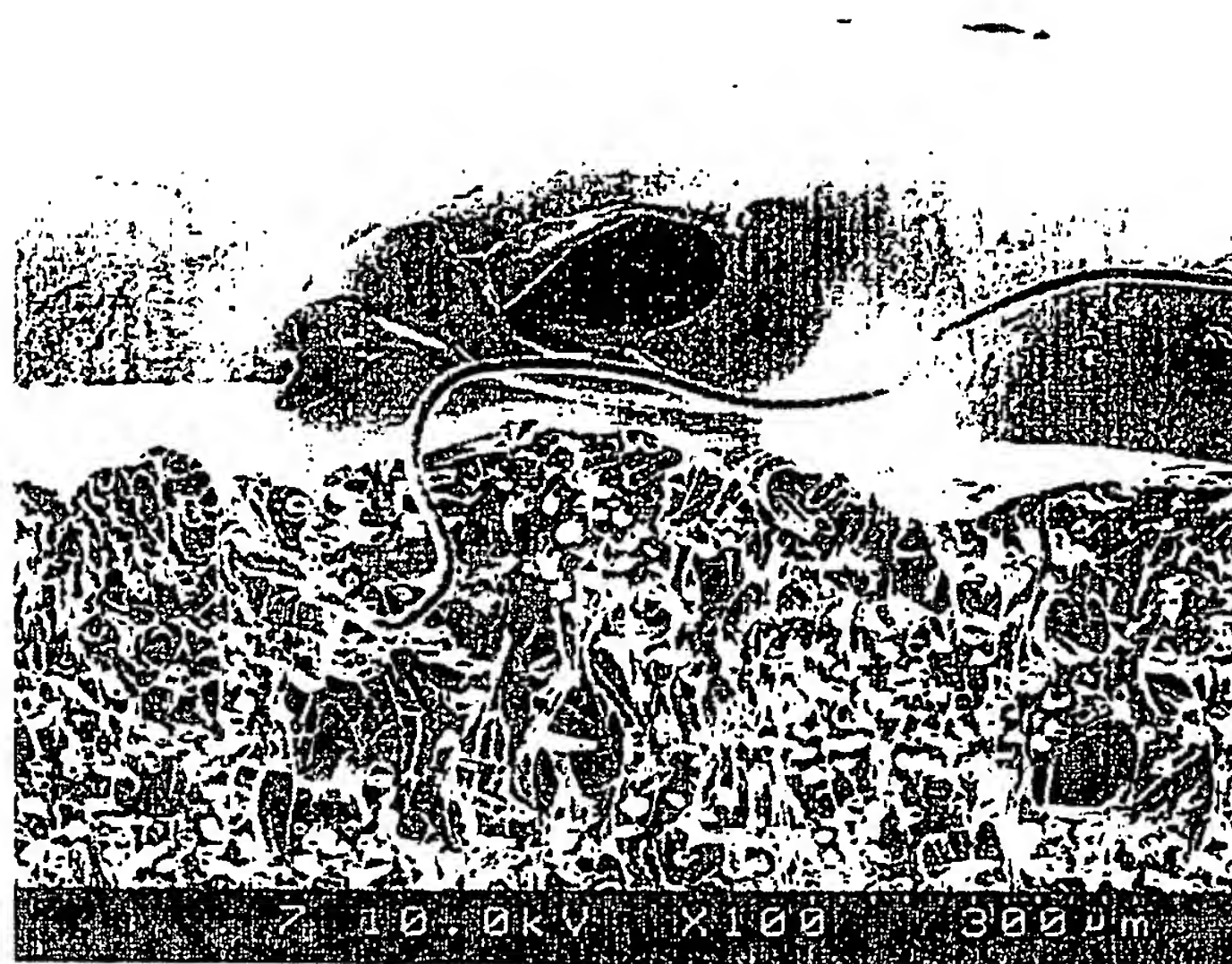


FIG. 18



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FIG. 19



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR01/01724

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08L 75/04, D06N 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08L 75/04, D06N 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and Applications for Inventions since 1975

Korean Utility Models and Applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NPS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 99-75812 A (Daewoo Co., Ltd) 15 October 1999 see the whole document	1-8
Y	US 4,171,391 A (Wilmington Chemical Corp.) 16 October 1979 see the whole document	1-8
A	KR 98-14449 A (Daewoo Co., Ltd) 25 May 1998 see the whole document	1-8

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 FEBRUARY 2002 (22.02.2002)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 920 Dunsan-dong, Seo-gu,
Daejeon Metropolitan City 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer

BAHN, Yong Byung

Telephone No. 82-42-481-5547

